

# RESERVE COPY PATENT SPECIFICATION

680,710

Inventors:—ALFRED LOUIS HOCK and JOHN ALEXANDER DUKES.



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## COMPLETE SPECIFICATION.

### Production of Manganous Chloride.

We, MAGNESIUM ELEKTRON LIMITED, a British Company, of Lumm's Lane, Clifton Junction, near Manchester, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of manganous chloride.

According to the present invention manganous chloride is produced by reacting chlorine gas with manganese or an alloy thereof in a refractory lined container having a base which is so inclined that the fused chloride drains away from the metal or alloy as it is produced.

The manganous chloride is not appreciably volatile at the operating temperatures. Any iron present in a manganese alloy may be substantially removed as ferric chloride because of its higher volatility.

The main difficulties which arise in the preparation of manganous chloride by the interaction of chlorine gas with the metal or ferromanganese are caused by the tendency of the chloride to coat the surface of the metal or alloy and thereby to interfere with the progress of the reaction. The chloride must therefore be allowed to drain away continuously from the zone of reaction. However, if the charge of metal or alloy be arranged in a vertical apparatus to facilitate such drainage, the metal or alloy at the base of the apparatus may sinter although its temperature may be well below the melting point and the removal of any unreacted charge becomes a matter of great difficulty. We have found that if the reaction is carried out in a refractory lined container having a suitably inclined base an unexpectedly satisfactory result can be obtained.

In carrying out the present invention we may arrange for a flow of the chlorine gas

in the same direction as the flow of the fused chloride so that the removal of the fused chloride from the surface of the metal or alloy is assisted by the inflow of gas. This is particularly desirable because there is a considerable increase in the volume of the material as the metal or alloy reacts with the chlorine gas and the chloride must be rapidly removed from the reaction zone. It results also in an easy maintenance of a suitable reaction temperature within the apparatus since the inflow of gas can readily be controlled and its even distribution ensured in order that the heat generated by the reaction can be continuously dissipated at the desired rate through the walls of the reaction vessel and by the sensible heat of the products of reaction.

The invention will now be further described by way of example with reference to the accompanying diagrammatic drawing which is an axial vertical section of an apparatus suitable for carrying out the invention.

A container is constituted by a refractory lined steel shell forming an inclined tube 10, and is supported by annular runners 11, 12, on rollers 13, 14, at an angle of about 8 to 24 degrees. The upper end has an end-plate 3 provided with a gas inlet tube 4 connected to a flexible feed pipe 5, and a feed hopper for introducing the metal charge. The lower end of the container has an end-plate 6 provided with a hole 12 for the escape of the reaction products, and an opening 14 for inspection. An exhaust system 7 removes the waste products issuing from the container. A charge of metal is shown at 9.

The slope of the container is arranged so that the fused chloride flows freely away from the charge yet not so steeply that the charge sinters excessively during reaction. The thickness of the refractory lining of the reaction tube is advantageously adjusted

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so that for any desired rate of reaction the excess heat is dissipated through the walls without the centre of the charge becoming overheated, the temperature of the fused chloride being maintained above its melting point. The residues left in the tube may be removed from either end according to convenience. It is sometimes advantageous to rotate the container during the course of the reaction to maintain a high rate of production or to maintain the quality of the product according to the nature of the changes which occur within the tube during the course of the reaction. The rotation may be continuous or intermittent.

As an example of the manner in which this invention may be used we will now describe a method of producing manganous chloride from ferromanganese and gaseous chlorine. The tube 10 has an internal diameter of 16" and a length of 4' 6" and is charged with 5 cwts. of ferromanganese in lumps of up to 3" size. The lower part of the charge is heated to red heat with a gas burner and doors at the ends of the tube are then immediately closed. Chlorine is at once passed in through the pipe 5 at the upper end while fused manganous chloride is allowed to flow from the opening 12. The chlorine input rate is maintained at 20 to 50 lbs. per hour dependent upon the temperature of the reaction until the chlorine is no longer being consumed efficiently.

If the temperature within the tube becomes too low, e.g. 600° C., the manganous chloride is no longer fluid. If the temperature becomes too high, e.g. 1000° C., the manganous chloride is appreciably volatilised and the ferromanganese begins to soften. The tube is rotated a half-turn on its rollers

every two hours for a period of about 20 hours by which time about 7 cwts. of manganous chloride will have been produced. A substantial proportion of the iron in the ferromanganese consumed is evolved as volatile ferric chloride. Any undesirable amount of ferrous chloride which may pass out with the manganous chloride may be removed in whole or in part by introducing a subsidiary stream of chlorine into the apparatus near to the outlet hole and/or by treatment of product in a separate apparatus. The residue left in the reaction tube may be contaminated on its outer surface with carbon which was originally present in the ferromanganese and this may be removed for example by washing with water so that the unreacted metal may be returned to the apparatus for further chlorination.

What we claim is:—

1. A process for the production of manganous chloride wherein chlorine gas is reacted with manganese or ferromanganese in a refractory lined container having a base which is so inclined that the fused chloride drains away from the metal or alloy as it is produced.

2. A process as claimed in Claim 1 in which the chlorine gas is caused to flow in the container in the same direction as the flow of the manganous chloride.

3. A process as claimed in Claim 1 and substantially as described with reference to the accompanying drawings.

For the Applicants:  
S. E. MATTHEWS,  
Chartered Patent Agent,  
31 and 32, Bedford Street, Strand,  
London, W.C.2.

## PROVISIONAL SPECIFICATION.

### Production of Fusible Metallic Halides.

75 We, MAGNESIUM ELEKTRON LIMITED, a British Company, of Lumm's Lane, Clifton Junction, near Manchester, do hereby declare the nature of this invention to be as follows:—

80 This invention relates to the production of fusible metal halides.

According to the present invention fusible metal halides are produced by reacting halogen gas with a metal or alloy of higher melting point than the halide in a container having a base which is so inclined that the fused halide drains away from the metal or alloy as it is produced.

90 The present invention involves processes in which metallic halides are prepared that are not appreciably volatile at the operating

temperatures. Any iron present as an alloy of the metal may be substantially removed as ferric halide because of its higher volatility. It will be appreciated that the invention is therefore distinguished from known processes in which alloys of iron with metals of which the chlorides are required are reacted with chlorine and in which the required metal chloride is more volatile than iron chloride and in which the separation of the required metal chloride is based upon the lower volatility of the iron chloride or upon a fractional distillation as for example with ferrotitanium or ferrovandium.

It is also important for the purpose of the present invention that the metal or alloy from which the halide is to be made shall have a higher melting point than that of the

halide. The exact magnitude of the difference by which the melting point of the metal or alloy must exceed the melting point of the halide is not of special importance but is rather dependent upon the degree of temperature control attainable in the plant in which the reaction is carried out.

It is known to produce metallic halides by the direct reaction of the halogen gas on the pure metal. The main difficulties which arise in the preparation of a fusible metallic halide by the interaction of the halogen gas with the metal or one of its alloys are caused by the tendency of the halide to coat the surface of the metal or alloy and thereby to interfere with the progress of the reaction. The halide must therefore be allowed to drain away continuously from the zone of reaction. However if the charge of metal or alloy be arranged in a vertical apparatus to facilitate such drainage, the metal or alloy at the base of the apparatus, being under some load from the charge above, may sinter because of the heat of the reaction although its temperature may be well below the melting point and the removal of any unreacted charge becomes a matter of great difficulty. We have found that if the reaction is carried out in a container having a suitably inclined base an unexpectedly satisfactory result can be obtained.

For the purpose of the present invention we may arrange for a flow of the halogen gas in the same direction as the flow of the fused halide so that the removal of the fused halide from the surface of the metal or alloy is assisted by the inflow of gas. This is particularly desirable because there is usually a considerable increase in the volume of the material as the metal or alloy reacts with the halogen gas and the halide must be rapidly removed from the reaction zone. It results also in an easy maintenance of a suitable reaction temperature within the apparatus since the inflow of gas can readily be controlled and its even distribution ensured in order that the heat generated by the reaction can be continuously dissipated at the desired rate through the walls of the reaction vessel and by the sensible heat of the products of reaction.

The invention will now be further described by way of example with reference to the accompanying diagrammatic drawing which is an axial vertical section of an apparatus suitable for carrying out the invention.

A container is constituted by a steel tube 10 lined with refractory brickwork 1 and is supported by suitable stanchions or framework (not shown) at an angle of about 12 to 24 degrees. The upper end has an end-plate 2 lined internally with asbestos and provided with a gas inlet tube 3 and a feed

hopper 4 for introducing the metal charge. The lower end of the container has an end-plate 5 lined with refractory bricks and provided with a hole 12 for the escape of the reaction products. A vessel 6 collects the fused halide. An exhaust system 7 removes the waste products issuing from either end of the container. A layer of inert material 8 is provided when required to filter the fused halide or to protect the end-plate 5. A charge of metal is shown at 9. Doors (not shown) may be provided in the end-plates.

The slope of the container is arranged so that the fused halide flows freely away from the charge yet not so steeply that the charge sinters excessively during reaction. The thickness of the refractory lining of the reaction tube is advantageously adjusted so that for any desired rate of reaction the excess heat is dissipated through the walls without the centre of the charge becoming overheated, the temperature of the fused halide being maintained above its melting point. The residues left in the tube may be removed from either end according to convenience. It is sometimes advantageous to rotate the container during the course of the reaction to maintain a high rate of production or to maintain the quality of the product according to the nature of the changes which occur within the tube during the course of the reaction.

As an example of the manner in which this invention may be used we will now describe a method of producing manganous chloride from the manganese alloy known as ferromanganese and gaseous chlorine. The steel tube 10 has an internal diameter of 15" and a length of 4' 6" and is lined with refractory brickwork about 3" thick. The tube is supported on rollers at an angle of 20° to the horizontal and charged with 5 cwts. of ferromanganese in lumps of up to 3" size. The lower part of the charge is heated to red heat with a gas burner and doors at the ends of the tube are then immediately closed. Chlorine is at once passed in through the pipe 3 at the upper end while fused manganous chloride is allowed to flow from the opening 12. The chlorine input rate is maintained at 20 to 50 lbs. per hour dependent upon the temperature of the reaction until the chlorine is no longer being consumed efficiently.

If the temperature within the tube becomes too low, e.g. 800° C., the manganous chloride is no longer fluid. If the temperature becomes too high, e.g. 1000° C., the manganous chloride is appreciably volatilised and the ferromanganese begins to soften. The tube is rotated a half-turn on its rollers every two hours for a period of about 20 hours by which time about 7 cwts.

of manganous chloride will have been produced. A substantial proportion of the iron in the ferromanganese consumed is evolved as volatile ferric chloride. Any undesirable amount of ferrous chloride which may pass out with the manganous chloride may be removed in whole or in part by introducing a subsidiary stream of chlorine into the apparatus near to the outlet hole and/or by treatment of the product in a separate apparatus. The residue left in the reaction tube may be contaminated on its outer surface with carbon which was originally

present in the ferromanganese and this may be removed for example by washing with water so that the unreacted metal may be returned to the apparatus for further chlorination.

Dated this 9th day of March, 1949.

For the Applicants:

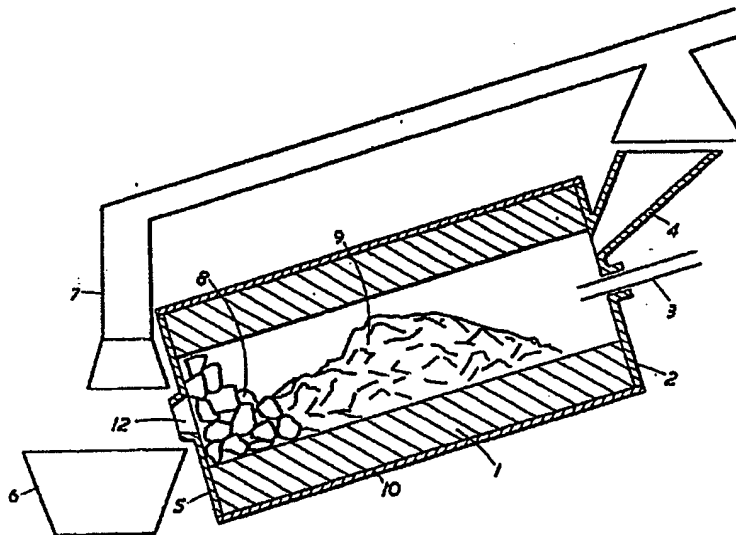
S. MATTHEWS,

Chartered Patent Agent,  
14-18, Holborn, London, E.C.1.

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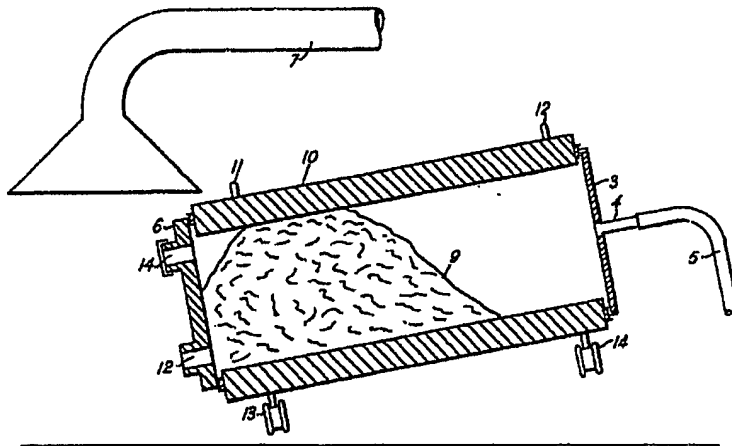
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